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"ISOTOPIC MASS BALANCE MEASUREMENTS FOR DETERMINATION OF COAL-DERIVED LIQUID CONTRIBUTION INTO REPROCESSING DISTILLATES"

by

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SUMMARY

Forestburg coal with $FeSO_4$ catalyst was co-processed under identical conditions with tetralin, hydrogenated anthracene oil, Athabasca pitch and a blend of Venezuelan vacuum resids. Also, for the latter two solvents the role of increasing coal loadings on product yield and make up was investigated.

Carbon isotopic mass balance was used to determine the fate of coal in these experiments. The results show that the solubilization of coal depends a great deal on the solvent. Coal loadings also play a role in determining the distribution of coal in synthetic products.

This report presents results from DSS contract between CANMET and the UNIVERSITY OF ALBERTA #23440 -7 - 9143/01- SS. It is divided into two sections and an appendix: PART A - The isotopic analyses and mass balance, PART B, the autoclave techniques and product work up. The appendix gives an abstract from this work submitted to the 39th Canadian Chemical Engineering Conference.

PART A

INTRODUCTION

Co-processing coal with bitumen, vacuum resids or other solvents yields a very complex slate of products. At some date coprocessing will be necessary to provide transportation fuels for Canada. Conventional analyses can give overall estimates of product yields from co-processing tests but fail to identify the contribution of coal to specific product fractions. Stable carbon isotope ($^{13}C/^{12}C$) monitoring of fuels and products, can however, by mass balance quantitatively determine the coal contribution to each fraction (1,2). Identifying quantitatively the proportion of coal to solvent in both the desired and undesired products will enhance the efficiency in designing bench, pilot and commercial co-processing units.

OBJECTIVES

The specific objectives in this study were to compare under identical autoclave run conditions, the solubilization of Forestburg coal in four solvents: Athabasca pitch,

vacuum resid blend - Blend 24, hydrogenated Anthracene oil (HAO) and tetralin. For the Athabasca and Blend 24 samples, the solubilization of coal as a function of coal loading (0, 10, 20, 30%) was also investigated. All experiments were loaded with the same concentration of $FeSO_4$. Details of the autoclave, run conditions and product work up are presented in Part B.

ISOTOPIC MASS BALANCE APPLIED TO CO-PROCESSING

If co-processing feeds differ in their natural $^{13}C/^{12}C$ ratio then the synthetic products would have intermediate isotopic ratios commensurate with their make up. A direct proportionality between isotopic shift and coal content is, however, not likely because during processing carbon-carbon bond breaking will induce kinetic isotopic shifts. In this study, therefore, both the Athabasca pitch and the Blend 24 were autoclaved individually as "blank runs" but under the same conditions as the co-processing tests. The isotopic compositions of their products served as one end member of the isotopic mass balance equation. Survey of literature indicates that the coal component does not need a "blank" correction (1).

ANALYTICAL TECHNIQUES

The feeds and end products were analyzed by conventional methods of stable isotope geochemistry. Approximately 20 mg sample were individually loaded into vycor tubes with ~ 2.5 g of "Cupox" (CuO) and thin slivers of Cu and Ag foil; frozen in liquid

nitrogen, evacuated and sealed. The tubes were placed in an 800°C oven for 12 to 24 hours and then cooled slowly. The tubes were broken open in a vacuum line and the combustion products extracted. The CO_2 was purified cryogenically and analyzed on a VG 602D stable isotope ratio mass spectrometer against a working laboratory standard. The determined isotope ratio was converted by the accepted factors to the internationally known PDB scale. During the course of this work, NBS-22 oil was also analyzed and it was found to have a $\delta^{13}C$ value of -28.65(‰).

The entire gas samples were collected from the autoclave in large plastic and mylar gas bags. Aliqots of the gas were combusted in partial vacuum over CuO at 800°C for isotopic analyses. The carbon content of all feeds and products was determined at the Microanalytical Laboratory, Department of Chemistry, University of Alberta.

DATA

Feeds

The isotopic analyses of the feeds are given in Table 1 as well as their carbon contents. The resolving power of ^{13}C - monitoring to determine coal content is directly proportional to the initial isotopic contrasts between feeds. In this study that difference is for Athabasca, 3.4‰; Blend 24, 1.2‰; HAO, 2.1‰, tetralin, 1.7‰. The expected

resolution is twice the error of analyses (±0.07‰) divided by the differences between feeds; ±4%, ±12%, ±7%, ±8%, respectively. The overall uncertainty on the total coal or solvent budget will be larger because the errors on each fraction will propogate to the total sum. In any case this study showed that even when the starting isotopic differences are small, useful information on the solubilitization of coal can still be obtained.

Blank Runs

Experiments 3 and 13 are autoclave runs with $FeSO_4$ catalyst and Athabasca pitch and Blend 24, respectively. The isotopic analyses of the run products are presented in Table 2. Inspection of the data reveal that indeed, isotopic partitionings are induced on the pitch and blend by processing. The observed effects are compatible with previously published analyses, with the gas and low temperature boiling distillates depleted of ^{13}C whereas the heavy end and IOM are enriched in ^{13}C. In detailed comparison, the Athabasca pitch did not produce a ^{13}C-depleted naptha, as does processing of raw Athabasca bitumen. Suprisingly though, the coal containing autoclave runs produced a ^{13}C-depleted naptha (see below).

Blend 24 produced a naptha 1‰ depleted of ^{13}C, a value larger than I would have anticipated. Also suprising is that the IOM from Blend 24 was lower in

^{13}C-content than the toluene soluble product.

Co-processing Runs

Isotopic analyses of the co-processed products are presented on Table 2. The percent of coal incorporated into each fraction can be calculated from the difference in isotopic composition between the coprocessed product and the coal divided by the difference between the isotopic composition in appropriate blank product and coal. In the case of Experiments 1 and 2, no "blank runs" were made and one uses the isotopic composition of tetralin and HAO. The calculated coal contents are listed in Table 3. Analogously, but independently, one can also calculate the fraction of solvent in each product. Results on solvent distribution are given in Table 4. On both Tables 3 and 4, the contribution of carbon to the crack gas was calculated by difference from the amount of crack gas produced in the blank. In the case of Experiment 1 it was assumed that all the crack gas came from coal and that a like amount was also generated in Experiment 2, with the excess coming from the HAO solvent. The isotopic analyses of the gases supports these assumptions.

In cases where nominally more than 100% or less than 0% contribution was calculated, only 100 or 0% were entered. By doing so, some minor information has been lost. Inspection of the isotopic data on the light distillates on Table 2 reveals a clear progression of δC^{13} values with increasing coal loadings (Experiments 4, 5, 7,

9, 10, 11) implying a progressive increase in the coal contribution. However, because the ^{13}C content of some of the "blanks" was less than that of the products, entries of 0% are given for coal contribution. The progression of the isotopic ratios indicates that the "blank" isotope ratio is inappropriate implying that the actual mechanisms of bond breaking in these bitumens is affected by the presence of coal.

TEST OF ISOTOPIC MASS BALANCE

Isotopic mass balance reveals the proportion of each feed in every product. But the amounts of products are quite variable. The amount of coal in each product can be determined by multiplying the weight of product recovered (Part B - Table 3) by their carbon content (Table 5) and the proportion of coal carbon in each fraction. Results from such calculations on coal distribution in the products are also entered on Table 3. Analogous calculations on solvent distribution are given on Table 4.

Given the calculated distribution of coal and solvent, one can sum the weight of carbon in the products and compare this with the weight of the feeds placed into the autoclave. This has been done on Table 6, both for coal and the solvents. The calculated yields range from 87 to 110%, but average 97%, proving that the carbon isotope mass balance can account for all the carbon in the feeds.

DISCUSSION

Inspection of Tables 2, 3 and 4 reveal quite a lot of complexity in the distribution of coal carbon in the products. Some observations to be examined more closely are the role of solvent, coal concentrations, residue or coke, and gas make up.

Role of Solvent

To simplify examining the role of solvent during co-processing the weights of coal in each product fraction from Table 2 have been normalized to percent of total coal charge incorporated into each fraction (Table 7).

The four solvents were all co-processed with coal at a 30% loading. Tetralin is the most effective solvent for coal. 63.1% of the coal charge was converted to distillate and 30.5% to extracts (mostly to toluene soluble) with only 5.2% remaining in the IOM. HAO was efficient, dissolving 47.3% of the coal into the four distillate fractions and 42.7% into the extracts, leaving 12% into the IOM. Athabasca pitch gave similar results to the HAO test (distillates, 47.3%; extracts, 37.6%; IOM, 15%) but with proportionately more coal in the high temperature distillate. Blend 24, yielded a significantly different distribution of coal in product with a small amount of coal (9.1%) being only detected in the naptha fraction. 63.8% of the coal went into the extracts but 26.8% remained in the IOM. As mentioned above, it is likely that some coal was incorporated into the other distillate fractions, but was not detectable from the isotopic analyses. In all tests the amount of

coal in the pentane soluble fraction was neglible. Coal in the toluene soluble fraction dominates the THF - soluble fraction by about a factor of two.

Role of coal concentration

The distribution of coal from the feed charge among products can be examined as a function of coal loadings for the Athabasca pitch and Blend 24 (Table 8). In this series of tests one can also examine the partitioning of the solvent feed among the product fractions.

Changing the coal loadings from 10 to 20 or 30% does not cause drastic changes in the pattern of coal incorporation. In the case of Athabasca Pitch, the fraction of coal charge in distillate increases from 37.9% to 40.4% and 47.3% respectively whereas the coal into extracts drops from 59.1% to 50.0 to 37.6%. However, the fraction of coal charge left in the IOM increases from 2.9% to 9.5% and 15% with increasing coal loadings. For Blend 24 the pattern is of the same nature but less marked. For distillate, 6.2% to 6.3% and 9.1%; extract 76.5% to 74.5% and 63.9%; IOM 17.3% to 19.3% 26.8% for the 10; 20 and 30% coal loadings.

When examining the distribution of solvent between product fractions one can also compare the relative weight of product from solvent determined isotopically from the co-processed tests with the actual weights of products from the "blank" runs. To a

first approximation, the upgrading of Athabasca Pitch and Bland 24 was not greatly affected by the increasing presence of coal. It appears though that in the tests with 30% coal loadings significantly more of both solvents was converted to distillate and less to extracts, but with increased solvent produced IOM.

IOM

Because of its deleterious nature IOM production in co-processing runs needs careful study. This study reveals that the IOM is not simply a residue from coal but also contains up to 57% carbon from the solvent (Table 4). The amount and make up of the IOM varies with solvent and coal loading. Its relative yield correlates with product distribution.

Gas Make

The gas make in the tests can contain up to 5% of the carbon of the charge. The isotope ratio of carbon of the total gas product varies systematically with solvent and coal loading indicating that the gas is derived both from coal and the solvent.

Inspection of the chemical composition of the gas (Part B - Table 2) reveals that the largest component by weight is CO_2. It is interesting to note that the amount of CO_2 increases with coal loadings but that the different solvents produce differing amounts of

CO_2: Tetralin, 1.58g; HAO, 4.92g; Athabasca Pitch, 3.06g; and Blend 24, 1.73g; all from tests with 30% coal loadings. Other systematic trends should be noted as well (CO, butane, propane etc). Isotopic analyses of separate chemical moieties would be most useful.

ACKNOWLEDGMENTS

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PART B

TABLE 1

ISOTOPIC COMPOSITION OF FEEDS: CARBON CONTENT OF FEE

	13 C (%) PDB	% CARBON
ATHABASCA PITCH	-28.54	81.9
BLEND 24	-26.39	85.27
TETRALIN	-23.47	90.98
HYDROGENATED ANTHRACENE OIL	-23.11	91.11
FORESTBURG COAL NORMAL	-25.18	64.52
FORESTBURG COAL CATALYZED	-25.17	58.17

TABLE 2

ISOTOPIC ANALYSIS OF PRODUCTS (‰PDB)

EXPERIMENT	1 TETRAL	2 HAO	3 (0)	4 (10)	5 (20)
DISTILLATE					
IBP-205 (N)	-23.60, -23.55	-25.62	-28.34	-29.62	-29.40
206-335(MD)	-24.26	-23.37	-28.99	-29.15	-28.85
336-415(LGO)	-25.43	-23.41	-28.97	-28.70	-28.45
416-525(HGO)	-25.20	-23.71	-28.86, -28.8	-28.38	-28.12
EXTRACT					
Pentane	-25.27	-24.82	-28.66	-28.53	-28.45
Toluene	-25.16	-24.97	-28.76	-28.02	-27.74
THF-sol	-25.01	-24.86	-28.39	-27.14	-26.70
I.O.M.	-24.80	-24.65	-28.21	-26.93	-26.89
GAS	-26.83	-30.05	-35.56, -36.0	-29.55	-32.57

EXPERIMENT	7 (30)	13 (0)	9 (10)	10 (20)	11 (30)
DISTILLATE					
IBP-205(N)	-29.18, -29.25	-27.29, -27.51, -27.41	-27.11	-26.92	-26.66
206-335(MD)	-28.53, -28.51	-26.22, -26.27	-26.33	-26.21	-26.03
336-415(LGO)	-28.08, -28.07	-25.46, -25.42, -25.4	-25.93	-25.79	-25.69
416-525(HGO)	-27.82, -27.82	-25.34, -25.50	-25.62	-25.54	-25.51
EXTRACT					
Pentane	-28.27, -28.27	-25.27, -25.43 -25.33	-25.51	-25.48	-25.40, -25.35
Toluene	-27.52, -27.55	-25.70, -25.67	-25.60	-25.46	-25.46, -25.36, -25.40
THF-sol	-25.67	-25.70	-25.49	-24.96, -25.07	-25.32, -25.24
I.O.M.	-26.29	-26.00, -26.05	-25.22	-25.02, -25.11	-25.31, -25.28
GAS		-33.22	-31.28	-31.07	-30.20, -29.86

TABLE 3

PERCENT OF COAL DERIVED CARBON IN PRODUCTS;
GRAMS OF COAL DERIVED CARBON IN PRODUCTS*

EXPERIMENT	1		2		4	
	% COAL-C	COAL WT: g	% COAL-C	COAL WT: g	% COAL-C	COAL WT: g
DISTILLATE						
N	6.2	4.69	100	1.66	0	0
MD	46.3	10.25	12.6	6.80	0	0
LGO	100	3.49	14.6	2.74	7.1	1.00
HGO	100	1.78	29.1	1.61	13.3	3.19
EXTRACT						
PENTANE	100	0.48	82.8	0.62	3.7	0.65
TOLUENE	100	6.63	90.1	7.69	20.6	5.66
THF - SOL	90.3	2.68	84.7	3.77	34.6	0.21
IOM	78.00	1.99	74.6	3.40	42.2	0.32
GAS		1.32		3.83		0.5

* Calculated by multiplying weight of product x % carbon content x % coal-c.

TABLE 3

EXPERIMENT	5		7		9	
	% COAL-C	COAL WT: g	% COAL-C	COAL WT: g	% COAL-C	COAL WT: g
DISTILLATE						
N	0	0	0	0	13	0.59
MD	3.7	0.78	12.1	2.48	0	-
LGO	13.7	1.86	23.5	3.17	0	-
HGO	20.3	4.38	28.4	6.84	0	-
EXTRACT						
PENTANE	6.00	1.23	11.2	0.46	0	-
TOLUENE	28.5	4.25	34.6	7.12	17.5	3.95
THF - SOL	34.6	2.11	84.6	2.36	87.5	3.31
IOM	43.5	1.65	63.3	3.97	94.7	1.64
GAS		1.08		2.07		

TABLE 3

EXPERIMENT	10		11	
	% COAL-C	COAL WT: g	% COAL-C	COAL WT: g
DISTILLATE				
N	21.6	1.11	33.3	2.39
MD	0	-	0	
LGO	0	-	0	
HGO	0	-	0	
EXTRACT				
PENTANE	0	-	0	
TOLUENE	44.7	12.55	56.3	11.64
THF - SOL	100	0.49	64.8	5.16
IOM	100	3.37	85.2	7.03
GAS				

TABLE 4

**PERCENT OF SOLVENT DERIVED CARBON IN PRODUCTS;
GRAMS OF SOLVENT DERIVED CARBON IN PRODUCTS***

EXPERIMENT	1		2		4		5	
	% SOLVENT-C	SOLVENT WT.	% SOLVENT-C	SOLVENT WT.	% SOLVENT-C	SOLVENT WT.	% SOLVENT-C	SOLVENT WT.
DISTILLATE								
N	93.8	71.00	0	0	100	5.48	100	5.33
MD	53.7	11.85	87.4	58.25	100	23.88	96.3	20.02
LGO	0	0	85.4	22.99	92.9	13.19	86.3	11.69
HGO	0	0	70.9	3.93	86.7	20.97	79.7	17.21
EXTRACT								
PENTANE	0	0	17.2	0.13	96.3	16.96	94.00	19.28
TOLUENE	0	0	9.9	0.84	79.4	21.80	71.5	8.66
THF-SOL	9.7	0.29	15.3	0.68	65.4	0.4	47.7	2.91
IOM	22	0.90	25.4	1.16	57.8	0.43	56.5	2.14
GAS	0	0		3.83		3.71		3.71

* Calculated by multiplying weight of product x % carbon content x % solvent.

TABLE 4

EXPERIMENT	7		9		10		11	
	% SOLVENT-C	SOLVENT WT.	% SOLVENT-C	SOLVENT WT.	% SOLVENT-C	SOLVENT WT.	% SOLVENT-C	SOLVENT WT.
DISTILLATE								
N	100	5.74	87	3.97	78.4	4.03	66.7	4.78
MD	87.9	18.83	100	21.27	100	20.72	100	17.26
LGD	76.5	10.31	100	14.23	100	13.10	100	13.72
HGD	71.6	14.60	100	26.23	100	24.19	100	21.41
EXTRACT								
PENTANE	88.8	3.64	100	21.47	100	18.98	100	12.15
TOLUENE	65.4	13.45	82.5	18.61	55.3	26.70	43.7	9.04
THF-SOL	15.4	0.43	12.5	0.47	0	0	35.2	2.80
IOM	36.7	2.30	5.3	0.09	0	0	14.8	1.19
GAS		3.71		1.60		1.60		1.60

TABLE 5

% WT. CARBON IN PRODUCTS

RUN	N	MD	L00	H00	PS	TS	THFS	THFI
1	91.79	87.44	85.50	87.41	51.03	61.56	74.36	48.53
2	87.69	90.74	92.41	91.70	43.43	84.62	81.86	53.79
3	82.58	84.42	85.42	85.15	85.39	83.30	84.57	37.49
4	82.83	83.92	84.06	84.43	85.08	84.10	77.02	28.65
5	82.09	83.67	84.16	84.84	86.27	85.25	76.18	27.32
7	79.94	83.50	84.17	84.64	86.53	79.37	72.45	29.67
9	84.44	85.48	85.70	86.28	83.03	80.75	78.57	70.54
10	82.33	84.80	85.65	85.75	84.75	84.23	79.59	64.23
11	81.67	84.20	85.36	85.57	85.91	82.04	81.77	63.39
13	84.80	86.37	86.45	86.25	85.94	84.15	89.43	73.31

TABLE 6

CARBON INVENTORY BASED ON ISOTOPE MASS BALANCE*

EXPERIMENT	FEED (g)		PRODUCTS (g)		% YIELD		
	COAL-C (θ)	SOLVENT-C	COAL-C (θ)	SOLVENT-C	COAL-C	SOLVENT-C	TOTAL
1	32.51	95.57	34.38	86.77	105.7	90.7	95
2	32.51	95.58	34.36	91.08	105.7	95.3	97.9
4	10.85	112.79	11.75	108.87	108.3	96.5	97.6
5	21.73	100.44	19.00	93.73	87.4	93.3	92.3
7	32.57	87.64	29.59	75.89	90.8	86.6	87.7
9	10.49	115.11	11.03	113.04	105.2	98.2	98.8
10	21.46	103.33	19.8	113.4	92.3	109.7	106.7
11	32.48	90.39	30.66	87.55	94.4	96.9	96.2
					AVE. 98.7	95.9	96.5

* Normalized to 100% recovery from autoclave.

TABLE 7

FATE OF COAL CHARGE IN VARIOUS PRODUCTS (30% COAL FEED RUNS) AS FUNCTION OF SOLVENT.

EXPERIMENT	TETR 1	HAO 2	ATHABASCA 7	BLEND 24 11
DISTILLATE				
N	14.7	5.9	0	9.1
MD	32	24	9.4	-
LGO	10.9	9.6	12	-
HGO	5.5	5.7	25.9	-
SUB-TOTAL(%)	*63.1*	*45.2*	*47.3*	*9.1*
EXTRACT				
PS	1.5	2.2	1.7	-
TS	20.7	27.2	27	44.4
THFS	8.3	13.3	8.9	19.5
SUB-TOTAL(%)	*30.5*	*42.7*	*37.6*	*63.9*
IOM	6.2	12	15	26.8

TABLE 6

FATE OF COAL CHARGE IN VARIOUS PRODUCTS AS FUNCTION OF COAL CONCENTRATION.

	BLEND-24			ATHABASCA		
COAL FEED(%)	10	20	30	10	20	30
EXPERIMENT	9	10	11	4	5	7
DISTILLATE						
N	6.2	6.3	9.1	-	-	-
MD	-	-	-	-	4.5	9.4
LGO	-	-	-	9	10.7	12
HGO	-	-	-	28.9	25.2	25.9
SUB-TOTAL (%)	*6.2*	*6.3*	*9.1*	*37.9*	*40.4*	*47.3*
EXTRACT						
PENT	-	-	-	5.9	7.1	1.7
TOL	41.6	71.8	44.4	51.3	24.5	27
THF	34.9	2.8	19.5	1.9	18.4	8.9
SUB-TOTAL (%)	*76.5*	*74.5*	*63.9*	*59.1*	*50*	*37.6*
IOM	17.3	19.3	26.8	2.9	9.5	15

TABLE 9

FATE OF SOLVENT IN VARIOUS PRODUCTS AS FUNCTION OF COAL CONCENTRATION.

	ATHABASCA				BLEND 24			
COAL FEED (%)	0	10	20	30	0	10	20	30
EXPERIMENT	3	4	5	7	13	9	10	11
DISTILLATE								
N	5.1	4.6	5.7	7.6	7.1	3.5	3.6	5.5
MD	22.2	21.9	21.4	24.8	21.2	18.8	18.3	19.7
LGO	12.3	12.1	12.5	13.5	10.9	12.6	11.5	15.6
HGO	17.8	19.3	18.4	19.2	20.5	23.2	21.3	24.5
SUB-TOTAL (%)	*57.4*	*57.9*	*58*	*65.1*	*59.7*	*58.1*	*54.7*	*65.3*
EXTRACT								
PENT	9.3	15.5	20.6	4.7	9.1	19	16.7	13.9
TOL	26.1	20	9.2	17.7	21.4	16.4	23.5	10.3
THF	0.5	0.3	4.3	0.6	0	0.4	0	3.2
SUB-TOTAL (%)	*36.3*	*36.2*	*36.4*	*23*	*30.5*	*35.8*	*40.2*	*27.4*
IOM	0.4	0.4	2.3	3	1.8	0	0	1.3

PART B

COPROCESSING OF COAL AND PETROLEUM PITCH

BY

K. BADREE AND T. OHUCHI

Final Report for Work Performed under
Activity #602204201 of Project:

UNIVERSITY OF ALBERTA (PROF. K. MUEHLENBACHS)

JANUARY 1989

SUMMARY

This report contains the yield results of ten autoclave experiments of the contract between Prof. K. Muehlenbachs and Coal and Hydrocarbon Processing Department, Alberta Research Council. All identification numbers in Tables correspond to those of products identified on sample bottles and gas bags, which were delivered to the isotope laboratory. Also, the details of autoclave experimental and work-up procedure were described. Both feedstocks and experimental conditions were provided by Dr. P. Rahimi, CANMET.

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1.0 OBJECTIVES AND BACKGROUND

The objectives in this contract were:

1. To perform ten autoclave experiments, using a one litre autoclave and
2. To isolate product slurries in the following fractions:
   - gas components
   - water
   - distillates (IBP-205, 206-335, 336-415 and 416-525°C)
   - extracts (pentane, toluene and THF solubles and THF insolubles)

In addition, in order to assess pitch and coal conversions the amounts of -524°C fraction in Athabasca and Blend 24 feeds by distillation and IOM in THF insolubles by proximate analyses were measured.

Consequently, to provide isolated samples and companion yield data from experiments constituted the contract.

Both feedstocks and experimental conditions were provided by Dr. P. Rahimi, CANMET.

2.0 EXPERIMENTS

2.1 MATERIALS

Feedstocks supplied by P.Rahimi are as follows:

- Athabasca pitch
- Blend 24
- Normal coal
- Catalyzed coal

Normal coal was dried under vacuum at 80°C for four hours. The results of proximate analysis were moisture 33 wt% and ash 8.1 wt%, respectively. The rest of the samples were used as received.

Reagent grade pentane, toluene, THF and iron sulphate ($FeSO_4$) anhydrous were obtained from Terochem Laboratory.

2.2 AUTOCLAVE EXPERIMENT AND PRODUCT WORK-UP PROCEDURE

All tests were carried out in a one litre stirred autoclave, manufactured by Autoclave Engineers. The autoclave was equipped with a stirrer, a cooling coil and a thermowell. A baffle was placed inside the autoclave to enhance contact between the slurry and gas phases. A simplified process flow diagram of the unit is shown in Figure 1. It took approximately 50 min. (8°C/min) to heat the reactants from room temperature to reactor temperature of 430°C with stirring at 800 rpm. When the reaction temperature was achieved, cold water was introduced periodically via the cooling coil to maintain this reaction temperature ($\pm$1°C). The reaction time for all tests was 45 minutes. After the reaction was completed, the autoclave was allowed to cool down to 120°C and at an rpm of 100. The gases were vented through a cold trap and its volume measured by a dry gas meter, and collected in a one hundred litre gas bag. A small sub-sample of gas was taken for G.C. analysis, the rest was sent for isotope analysis. The cold trap which was Tared, was weighed and its contents were collected.

The product from the autoclave was pipetted out into a 500 ml distillation flask. The autoclave and its accessories were thoroughly washed out with methylene chloride and this solvent was removed via a roto-vap. The above three portions were combined for distillation. An atmospheric distillation (ASTM D-86) was performed and the end point was 205°C. At end point the vapor temperature was held for ten minutes. The water was separated from the naphtha using a phase separator filter paper. When the pot cooled down to room temperature, a vacuum distillation (ASTM D1160) was performed using a Hi-Vac Still manufactured by H.S. Martin. Three cuts were fractionated: a) middle distillate (206-335°C), b) light gas oil (336-415°C), c) heavy gas oil (416-525°). At each end point, the vapor temperature was held for 10 minutes. The residue was freezed dried with liquid nitrogen and transferred into a Whatman's Cellulose Extraction thimble, placed in a Soxhlet and extracted for twenty-four hours with pentane. After extraction, the thimble was removed from

the Soxhlet and dried in an oven set at 200°C for twenty-four hours. The extract was placed in a roto-vap to remove the solvent. After solvent removal, the extract was also dried for twenty-four hours in an oven at 200°C. This step was repeated for both toluene and THF extraction. When the THF extraction was completed the thimble was dried, the content was removed for proximate analysis. Figure 2 illustrates the analyzed schematic for product work-up procedure.

3.0 RESULTS

All the data required to this contract are summarized in the following tables:

Table 1 Autoclave Charge
Table 2 Product Gas Distribution
Table 3 Organic Mass Balance
Table 4 Residue Analysis and Coal Conversion
Table 5 Pitch Conversion
Table 6 Hydrogen Consumption
Table 7 Ash Balance

4.0 ACKNOWLEDGEMENT

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TABLE 1

AUTOCLAVE CHARGE

Wt. g

Run #	1	2	3	4	5	7	13	9	10	11
Coal Conc. wt%	30	30	0	10	20	30	0	10	20	30
Solvent	Tetralin	HAO	Athabasca Bitumen				Blend #24			
	105.04	104.91	152.08	137.72	122.64	107.01	150.10	134.99	121.18	106.01
Cat. Coal	13.15	13.20	-	18.66	17.78	13.18	-	18.03	17.40	13.10
Norm. Coal	38.53	38.48	-	-	17.66	38.60	-	-	17.58	38.53
$FeSO_4$	-	-			-	-			-	-

TABLE 2

PRODUCT GAS DISTRIBUTION Wt g

Run #	1	2	3	4	5	7	13	9	10	11
Hydrogen	3.07	2.75	2.94	3.05	3.05	3.14	3.54	2.62	2.60	2.53
Propane	0.23	1.18	0.94	0.98	1.08	1.28	0.48	0.24	0.51	0.69
Propylene	0.02	0.11	0.12	0.12	0.11	0.09	0.06	0.02	0.07	0.06
Isobutane	0.02	0.21	0.23	0.22	0.21	0.23	0.09	0.04	0.17	0.16
Butane	0.05	0.74	0.59	0.63	0.64	0.69	0.18	-	0.44	0.40
Butenes	0.02	0.11	0.14	0.16	0.15	0.18	0.05	0.04	0.13	0.10
Iso-Pentane	0.01	0.16	0.16	0.18	0.21	0.19	0.05	0.01	0.14	0.11
Pentane	0.01	0.21	0.21	0.23	0.29	0.27	0.06	0.01	0.18	0.15
CO_2	1.58	4.92	0.06	0.85	1.69	3.06	0.03	0.27	1.10	1.73
Ethylene	-	0.02	0.03	0.05	0.03	0.02	0.01	0.01	0.01	0.01
Ethane	0.27	1.00	1.02	1.08	1.11	1.41	0.47	0.30	0.60	0.67
Methane	0.35	0.88	1.13	1.20	1.33	1.64	0.55	0.58	0.81	0.90
CO	0.24	0.26	0.06	0.23	0.46	0.53	0.02	0.10	0.26	0.31
H_2S	0.01	0.12	2.31	2.31	1.84	1.96	0.24	0.08	0.48	0.48
TOTAL	5.88	12.67	9.94	11.29	12.20	14.69	5.83	4.32	7.50	8.30

TABLE 3

ORGANIC MASS BALANCE (wt g)

Run #	1	2	3	4	5	7	13	9	10	11
INPUT										
Solvent	105.04	104.91	150.41	136.21	121.29	105.84	150.10	134.87	121.07	106.00
Cat. Coal	10.91	10.95	-	15.48	14.75	10.85	-	14.95	14.43	10.86
Norm. Coal	34.24	34.20	-	-	15.69	34.22	-	-	15.62	34.24
TOTAL g	150.19	150.06	150.41	151.69	151.73	150.91	150.10	149.82	151.12	151.10
OUTPUT										
DISTILLATE										
Water	4.75	5.19	2.82	3.57	5.01	5.04	3.53	3.08	5.25	6.67
IBP-205	82.46	1.90	7.58	6.62	6.49	7.18	10.75	5.40	6.24	8.78
206-335	25.24	73.45	32.36	28.45	25.11	25.66	31.49	24.88	24.43	20.51
336-415	4.08	29.13	17.78	16.82	16.09	16.01	16.09	16.61	15.29	16.07
416-525	2.04	6.05	25.77	28.43	25.45	24.09	30.37	30.40	28.24	25.02
TOTAL g	118.57	115.72	86.31	83.89	78.15	77.98	92.23	80.37	79.45	77.05
EXTRACT										
Pentane	0.94	1.73	13.36	20.70	23.78	4.74	13.62	25.86	23.80	14.14
Toluene	10.77	10.02	38.56	32.65	14.20	25.92	32.61	27.93	31.70	25.21
THF Sol.	3.99	5.44	0.61	0.79	8.04	3.85	0.07	4.81	0.61	9.73
I.O.M.	8.47	8.47	1.29	2.59	13.86	21.13	3.11	2.46	5.24	13.01
TOTAL g	24.17	25.66	53.82	56.73	59.88	55.64	49.41	61.06	61.35	62.09
GAS (EXCLUDING H_2)	2.81	9.92	7.00	8.24	9.15	11.55	2.29	1.70	4.90	5.77
TOTAL g	145.55	151.30	147.13	148.86	147.18	145.17	143.93	143.13	145.70	144.91
MASS BAL.%	96.9	100.8	97.8	98.1	97.0	96.2	95.9	95.5	96.4	95.9

TABLE 4

RESIDUE ANALYSIS AND COAL CONVERSION

RUN #	MOISTURE (WT%)	ASH (WT%)	RESIDUE (g)	IOM (g)	FEED DAF COAL (g)	CONV. (%)
1	0.7	35.0	13.13	8.47	45.15	81.2
2	0.7	35.5	13.26	8.47	45.15	81.2
3	0.4	65.7	3.78	1.29	-	-
4	0.3	60.0	6.50	2.59	15.48	83.3
5	0.5	26.0	18.87	13.86	30.44	54.4
7	0.5	28.6	29.74	21.13	45.07	53.1
13	0.1	19.9	3.89	3.11	-	-
9	0.5	48.3	4.81	2.47	14.95	83.5
10	0.7	40.5	8.92	5.27	30.05	82.5
11	0.3	26.7	17.83	13.03	45.10	71.1

TABLE 5

PITCH CONVERSION

119.6 of Athabasca Pitch was distilled using ASTM D1160 method. It contained 9.33% (11.19g) of -525°C fraction and 90.67% (108.77g) of +525°C fraction.

RUN #	Pitch + Coal (g)	+525 Fraction (g) (extract including IOM)	%Conversion
3	136.38	53.82	60.5
4	138.98	56.73	59.2
5	140.41	59.88	57.4
7	141.04	55.64	60.6

134.06g of Blend #24 contained 14.28% (19.15g) of -525°C fraction and 85.72% (114.91g) of +525°C fraction.

13	128.67	49.41	61.6
9	130.56	61.06	53.2
10	133.83	61.35	54.2
11	135.96	62.09	54.3

TABLE 6

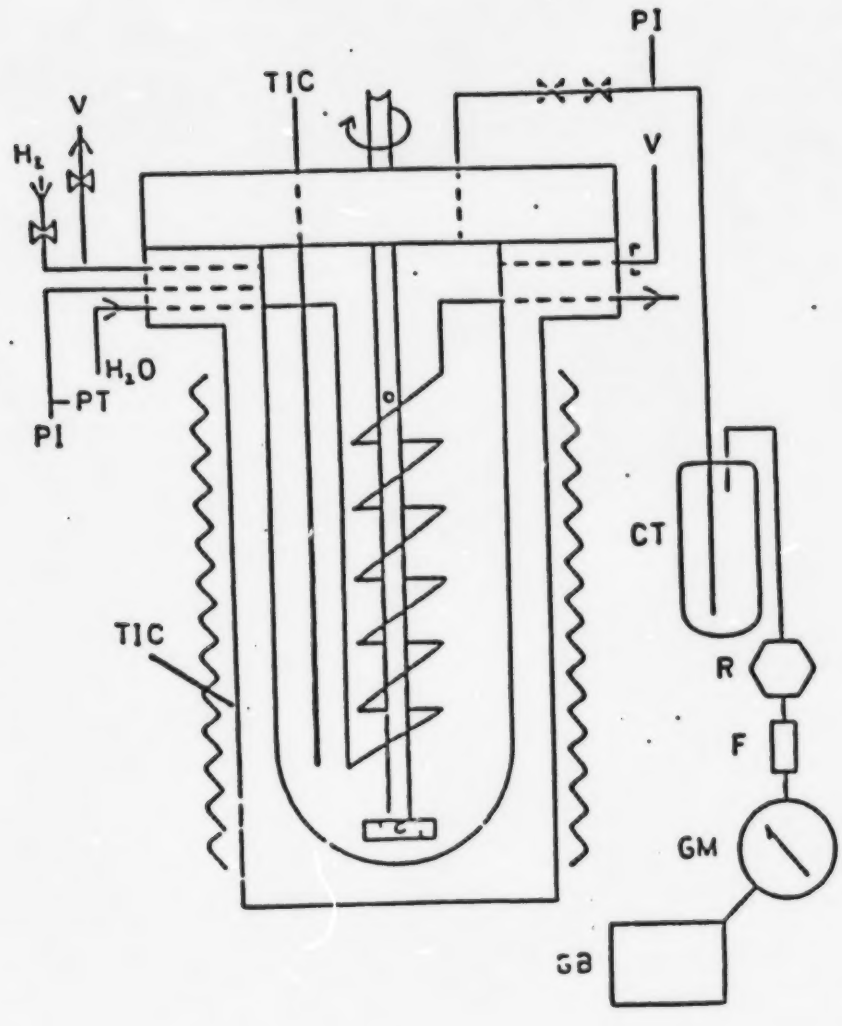
HYDROGEN CONSUMPTION (g)

RUN #	H_2 IN	H_2 OUT	WT CONSUMED
1	5.94	3.07	2.87
2	5.92	2.75	3.17
3	5.93	2.94	2.99
4	5.98	3.05	2.93
5	6.06	3.05	3.01
7	5.98	3.14	2.84
13	5.96	3.54	2.42
9	6.13	2.62	3.51
10	5.97	2.60	3.37
11	5.85	2.53	3.32

TABLE 7

ASH BALANCE

RUN #	ASH IN (g)	ASH OUT (g)	BALANCE (%)
1	6.53	4.66	71.4
2	6.53	4.79	73.4
3	3.40	2.49	73.2
4	4.95	3.91	79.0
5	6.35	5.01	78.9
7	7.88	8.61	109.0
13	1.74	0.78	44.8
9	3.46	2.34	67.6
10	5.04	3.65	72.4
11	6.54	4.80	73.4



CT = cold trap
F = filter
GM = gas meter
GB = gas bag
PT = pressure transducer
PI = pressure indicator
TIC = thermocouple
V = vent

Figure 1 One-Litre Autoclave System

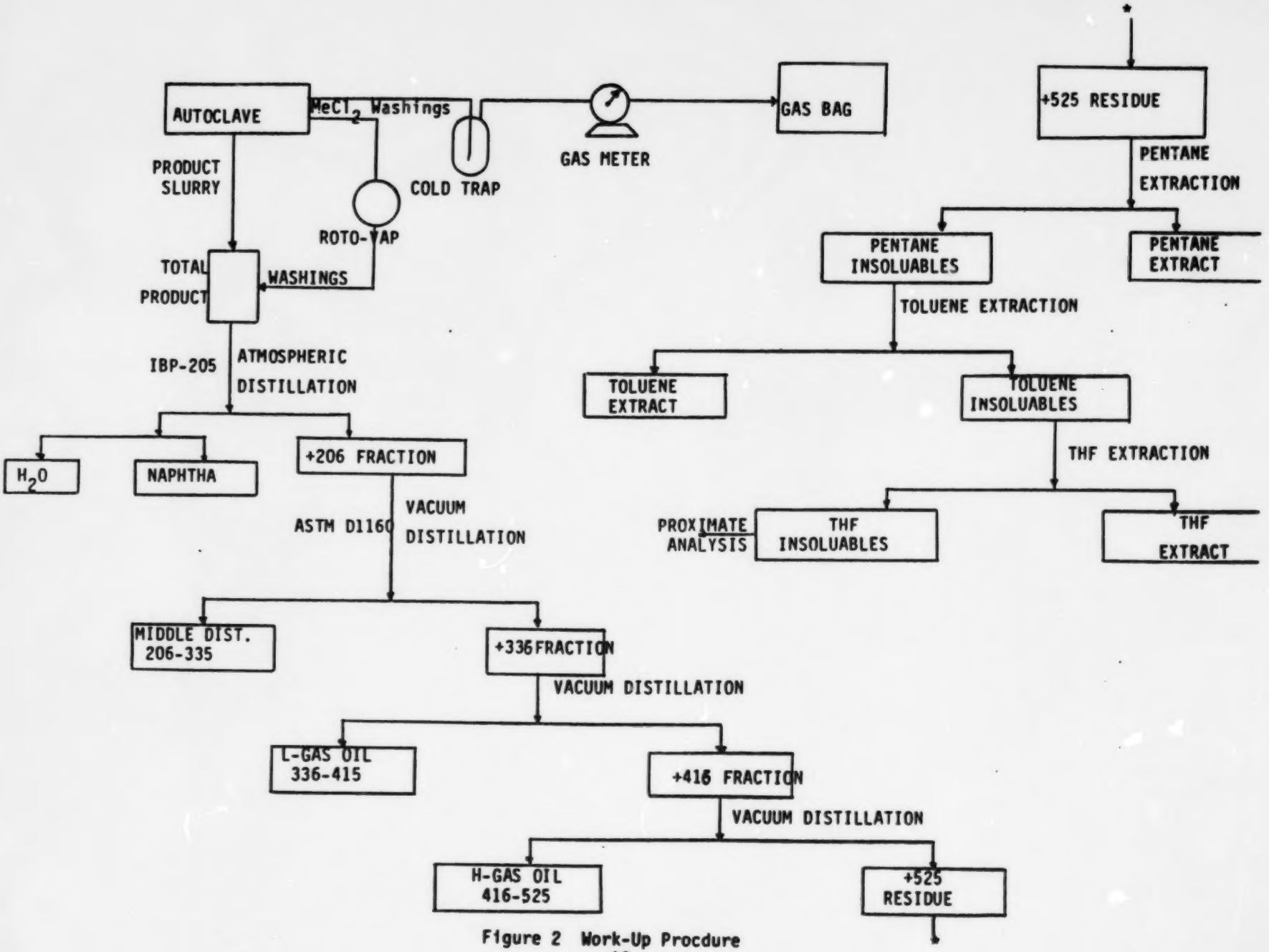


Figure 2 Work-Up Procdure